

Rec'd PCT/EP 05 MAY 2005

PCT/EP 03 / 12166

EP 03 / 12166

Europäisches  
Patentamt

European  
Patent Office

Office européen  
des brevets

REC'D 05 DEC 2003

WIPO

PCT

Bescheinigung

Certificate

Attestation

Die angehefteten Unterla-  
gen stimmen mit der  
ursprünglich eingereichten  
Fassung der auf dem näch-  
sten Blatt bezeichneten  
europäischen Patentanmel-  
dung überein.

The attached documents  
are exact copies of the  
European patent application  
described on the following  
page, as originally filed.

Les documents fixés à  
cette attestation sont  
conformes à la version  
initialement déposée de  
la demande de brevet  
européen spécifiée à la  
page suivante.

Patentanmeldung Nr. Patent application No. Demande de brevet n°

02079646.2

**PRIORITY DOCUMENT**  
SUBMITTED OR TRANSMITTED IN  
COMPLIANCE WITH  
RULE 17.1(a) OR (b)

Der Präsident des Europäischen Patentamts;  
Im Auftrag

For the President of the European Patent Office

Le Président de l'Office européen des brevets  
p.o.



R C van Dijk

**BEST AVAILABLE COPY**



Anmeldung Nr:  
Application no.: 02079646.2  
Demande no:

Anmeldetag:  
Date of filing: 05.11.02  
Date de dépôt:

Anmelder/Applicant(s)/Demandeur(s):

Akzo Nobel N.V.  
Velperweg 76  
6824 BM Arnhem  
PAYS-BAS

Bezeichnung der Erfindung/Title of the invention/Titre de l'invention:  
(Falls die Bezeichnung der Erfindung nicht angegeben ist, siehe Beschreibung.  
If no title is shown please refer to the description.  
Si aucun titre n'est indiqué se référer à la description.)

Fischer-tropsch catalyst composition

In Anspruch genommene Priorität(en) / Priority(ies) claimed / Priorité(s)  
revendiquée(s)  
Staat/Tag/Aktenzeichen/State/Date/File no./Pays/Date/Numéro de dépôt:

Internationale Patentklassifikation/International Patent Classification/  
Classification internationale des brevets:

B01J29/00

Am Anmeldetag benannte Vertragstaaten/Contracting states designated at date of  
filing/Etats contractants désignées lors du dépôt:

AT BE BG CH CY CZ DE DK EE ES FI FR GB GR IE IT LI LU MC NL PT SE SK TR

ACH 2970 PDEP

## FISCHER-TROPSCH CATALYST COMPOSITION

5 The present invention relates to a catalyst composition suitable for the conversion of carbon monoxide and hydrogen to  $C_5^+$  hydrocarbon mixtures, comprising a Fischer-Tropsch catalyst component and an acidic component. The invention further relates to a process for the conversion of carbon monoxide and hydrogen to  $C_5^+$  hydrocarbon mixtures using this catalyst.

10 It is known to convert carbon monoxide and hydrogen to larger hydrocarbons using a composition comprising a Fischer-Tropsch catalyst component and an acidic component.

For instance, US 4,595,702 discloses a Fischer-Tropsch process using a copper-containing iron catalyst as Fischer-Tropsch catalyst component and a  
15 zeolite selected from the group of ZSM-5, ZSM-45 and zeolite beta as the acidic component.

US 4,556,645 discloses the combined use of a Fischer-Tropsch catalyst component and a crystalline, microporous silicoaluminophosphate, non-zeolitic molecular sieve as the acidic component.

20 It has now been found that a fluid catalytic cracking (FCC) catalyst can be suitably used as solid acid component. This is a very favourable type of solid acid component, because it is less expensive than the above-mentioned solid acids. A spent FCC catalyst or an equilibrium catalyst (E-cat) is particularly  
25 favourable as it is even less expensive than fresh FCC catalyst.

Hence, the present invention relates to a catalyst composition suitable for the conversion of carbon monoxide and hydrogen to  $C_5^+$  hydrocarbon mixtures, comprising

- 30 (a) a Fischer-Tropsch catalyst component, and  
(b) a FCC catalyst component.

BEST AVAILABLE COPY

ACH 2970 PDEP

2

The term 'FCC catalyst' refers to any catalyst composition that can suitably be used in FCC processes. Any conventional FCC catalyst can be used in the process according to the invention. FCC catalysts generally contain zeolite Y, clay (e.g. kaolin, metakaolin, bentonite), silica, alumina, rare-earth metal compounds, etc.

Preferably, a metal compound is deposited on the FCC catalyst. Examples of suitable metals are rare earth metals, e.g. Ce, La, and transition metals of Groups IV-VIII of the Periodic System, e.g. V, Cr, Mn, Fe, Co, Ni, Cu, Zr, Nb, Ru, Re, etc.

This metal compound is preferably present in or on the FCC catalyst in amounts of 0.1 to 10 wt%, more preferably 0.3 to 2 wt%, calculated as oxide, and based on the total weight of metal-containing FCC catalyst.

The metal compound can be deposited on the FCC catalyst in any manner known in the art. Examples of such methods are impregnation, ion-exchange, and deposition precipitation of soluble metal salts.

If desired, the metal-deposited FCC catalyst is calcined after the metal compound has been deposited.

The advantage of using a spent FCC catalyst is that it is less expensive than a fresh FCC catalyst. Furthermore, as the hydrocarbon feed to be cracked in an FCC unit generally contains various metals, e.g. nickel, spent FCC catalyst may already contain the desired metal component, without performing an additional deposition step.

The Fischer-Tropsch catalyst component can be any conventional Fischer-Tropsch catalyst, preferably comprising iron and/or cobalt. For the preparation of such catalysts it is referred to, e.g., WO 01/97968, WO 01/89686/ and WO 01/70394.

The Fischer-Tropsch catalyst component can be promoted with various metals, e.g. Al, Ti, Cr, Mn, Ca, Na and/or K. Furthermore, the Fischer-Tropsch catalyst component can contain binder materials, such as silica and/or alumina.

BEST AVAILABLE COPY

ACH 2970 PDEP

3

The FCC catalyst component is present in the catalyst composition according to the invention in an amount of 5 to 40 wt%, more preferably from 10 to 30 wt%, based on the total weight of the catalyst composition.

- 5 The catalyst composition can be a physical mixture of Fischer-Tropsch catalyst component particles and FCC catalyst component particles. On the other hand, the catalyst composition can also comprise one type of particle, containing both the Fischer-Tropsch catalyst component and the FCC catalyst component together with a binder.

10

The invention further relates to a process for the conversion of carbon monoxide and hydrogen to  $C_5^+$  hydrocarbon mixtures, said process comprising contacting carbon monoxide and hydrogen with the above catalyst composition comprising a Fischer-Tropsch catalyst component and a FCC catalyst

15

component.

This process can be carried out in any suitable reactor, such as a (fixed) fluidised bed reactor.

20

The process is preferably a high-temperature Fischer-Tropsch process. The temperature ranges preferably from 250° to 400°C, more preferably from 300° to 370°C, and most preferably from 330° to 350°C. The pressure preferably ranges from 10 to 60 bar, more preferably 15 to 30 bar, and most preferably about 20 bar.

The  $H_2/CO$  volume ratio preferably ranges from 0.2 to 8.0, preferably 0.5-6, most preferably 1-3.

25

- The resulting hydrocarbon product preferably contains, on a mass basis, at least 35%, more preferably at least 45%, and most preferably at least 50% of  $C_5^+$  compounds. The process may be used for the production of aromatics, branched hydrocarbons, and/or olefins. Preferably, the process is used for the
- 30 production of liquid fuel, especially gasoline and preferably unleaded gasoline.

BEST AVAILABLE COPY

ACH 2970 PDEP

4

## CLAIMS

1. Catalyst composition suitable for the conversion of carbon monoxide and hydrogen to  $C_5^+$  hydrocarbon mixtures, comprising
  - (a) a Fischer-Tropsch catalyst component, and
  - (b) a fluid catalytic cracking catalyst component.
2. Catalyst composition according to claim 1 wherein the Fischer-Tropsch catalyst component comprises iron.
3. Catalyst composition according to claim 1 wherein the Fischer-Tropsch catalyst component comprises cobalt.
4. Catalyst composition according to any one of the preceding claims wherein the fluid catalytic cracking catalyst component is a spent fluid catalytic cracking catalyst.
5. Catalyst composition according to any one of the preceding claims wherein the fluid catalytic cracking component is a fluid catalytic cracking catalyst with a metal compound deposited thereon.
6. Catalyst composition according to claim 5 wherein the metal compound comprises a metal selected from the group consisting of Group IV metals, Group V metals, Group VI metals, Group VII metals, Group VIII transition metals, rare earth metals, and combinations thereof.
7. Catalyst composition according to any one of the preceding claims wherein the fluid catalytic cracking catalyst component is present in the catalyst composition in an amount of 5 to 40 wt% based on the total weight of the catalyst composition.

BEST AVAILABLE COPY

8. Process for the conversion of carbon monoxide and hydrogen to  $C_5^+$  hydrocarbon mixtures, said process comprising contacting carbon monoxide and hydrogen with a catalyst composition according to any of the claims 1-7.

ACH 2970 PDEP

6

Abstract

5 The present invention relates to a catalyst composition suitable for the conversion of carbon monoxide and hydrogen to  $C_5^+$  hydrocarbon mixtures. This catalyst composition comprises a Fischer-Tropsch catalyst component, and a fluid catalytic cracking (FCC) catalyst component.

Preferably, the fluid catalytic cracking catalyst is a spent FCC catalyst or an equilibrium catalyst.

BEST AVAILABLE COPY